

Document made available under the Patent Cooperation Treaty (PCT)

International application number: PCT/EP05/000697

International filing date: 21 January 2005 (21.01.2005)

Document type: Certified copy of priority document

Document details: Country/Office: EP
Number: 04075135.6
Filing date: 22 January 2004 (22.01.2004)

Date of receipt at the International Bureau: 24 February 2005 (24.02.2005)

Remark: Priority document submitted or transmitted to the International Bureau in compliance with Rule 17.1(a) or (b)



World Intellectual Property Organization (WIPO) - Geneva, Switzerland
Organisation Mondiale de la Propriété Intellectuelle (OMPI) - Genève, Suisse



Europäisches
Patentamt

European
Patent Office

Office européen
des brevets

Bescheinigung

Certificate

Attestation

Die angehefteten Unterla-
gen stimmen mit der
ursprünglich eingereichten
Fassung der auf dem näch-
sten Blatt bezeichneten
europäischen Patentanmel-
dung überein.

The attached documents
are exact copies of the
European patent application
described on the following
page, as originally filed.

Les documents fixés à
cette attestation sont
conformes à la version
initialement déposée de
la demande de brevet
européen spécifiée à la
page suivante.

Patentanmeldung Nr. Patent application No. Demande de brevet n°

04075135.6

Der Präsident des Europäischen Patentamts;
Im Auftrag

For the President of the European Patent Office

Le Président de l'Office européen des brevets
p.o.

R C van Dijk



Europäisches
Patentamt

European
Patent Office

Office européen
des brevets

PCT/EP2005/000697

21.01.05

Anmeldung Nr:
Application no.: 04075135.6
Demande no:

Anmeldetag:
Date of filing: 22.01.04
Date de dépôt:

Anmelder/Applicant(s)/Demandeur(s):

Akzo Nobel N.V.
Velperweg 76
6824 BM Arnhem
PAYS-BAS

Bezeichnung der Erfindung/Title of the invention/Titre de l'invention:
(Falls die Bezeichnung der Erfindung nicht angegeben ist, siehe Beschreibung.
If no title is shown please refer to the description.
Si aucun titre n'est indiqué se référer à la description.)

Stain blocking water borne coating composition

In Anspruch genommene Priorität(en) / Priority(ies) claimed / Priorité(s)
revendiquée(s)
Staat/Tag/Aktenzeichen/State/Date/File no./Pays/Date/Numéro de dépôt:

Internationale Patentklassifikation/International Patent Classification/
Classification internationale des brevets:

C09D7/00

Am Anmeldetag benannte Vertragsstaaten/Contracting states designated at date of
filing/Etats contractants désignées lors du dépôt:

AT BE BG CH CY CZ DE DK EE ES FI FR GB GR HU IE IT LU MC NL
PT RO SE SI SK TR LI

ANR 3030 PDEP

STAIN BLOCKING WATER BORNE COATING COMPOSITION

The invention relates to a water borne binder composition, a coating composition comprising the same, and a substrate which has been coated with
5 said coating composition.

Environmental legislation is the driving force behind the change from solvent borne coatings to water borne systems. Limits have been established for the amounts of volatile organic compound that are allowed in different coating
10 systems. The conventional solvent borne coating compositions were designed to be applied to the surfaces of certain substrates, including the surfaces of previously coated substrates. However, these substrates often contain water-soluble staining agents. So when water borne coatings are applied to such substrates, said staining agents can leach from the substrate into the coating,
15 thus causing discolouration thereof.

Staining agents are for example the water-soluble chromophoric compounds that are present in wood, such as tannins. These tannins can leach from the substrate into the coating, causing tannin staining, which appears as
20 discolouration on the surface of the coating. Such leaching can occur upon application or during the service life of the coating. Other staining agents that can leach from wood are terpenoid based resins or alkaloids such as chlorophorin. Yet other staining agents are salts contained in cementitious substrates. These salts can cause efflorescence or blooming, which is a
25 staining caused by the migration of the salt from the substrate to the paint coating, where it appears as white deposits.

Staining of the substrate and of coatings previously applied to the substrate can also be caused by sources external to the substrate. For example, cigarette smoke causes nicotine staining, which discolours light coloured coatings, and
30 inks from pens can cause marker stains on the substrate. When such stained substrates are (re)coated, this again can cause undesired discolouration of the

ANR 3030 PDEP

2

top coat. Each of the above-mentioned effects of staining is highly undesirable in coatings.

In attempts to improve the (tannin) stain blocking of water borne coatings
5 several approaches have been followed, which are described in the patent literature. Reactive pigments such as zinc oxide, aluminium zirconium phosphosilicate or barium phosphosilicate generally are quite effective in blocking stains caused by, for example, tannins. However, in practice they have some major drawbacks, since they can cause stability problems such as
10 viscosity increase and polymer gelation or coagulation. Obviously, this solution is limited to pigmented coatings. However, there is also a demand for clear stain blocking coatings. It is therefore desirable to obtain the tannin blocking properties without the use of reactive pigments.

15 In EP 0 849 004 an attempt was made to overcome the above-mentioned disadvantages by proposing a method for the tandem coating of wood substrates. This method comprises the application of two separate coatings, one of them a highly cross-linked coating and the other a cured coating formed from an aqueous coating composition. The cured coating is formed from an
20 aqueous composition comprising a carbonyl-functional polymer, preferably containing ethylene-ureldo-containing monomers.

Other attempts to resolve this problem include modifying the polymeric composition of the binder, for example by incorporating strong acids. US
25 2003/0073778 for instance describes an aqueous coating composition comprising from 0.1% to 10% by weight of at least one monomer bearing a pendant acid group having a pKa (in water at 20°C) of less than 4, and salts thereof. However, the incorporation of strong acid groups into the binder can lead to an increased hydrophilicity of the coating, resulting in decreased water
30 barrier properties.

ANR 3030 PDEP

3

In US 4,075,394 the application of an aqueous solution of a polyalkylene imine when treating tannin-containing surfaces is disclosed. Other approaches include the use of cationic latex polymeric binders and selected cationic pigment dispersants as described in for example US 5,312,863. The main drawback in
5 that case is the limited availability of paint ingredients that are cationic. All of the above-mentioned methods suffer from various disadvantages and fail to offer an adequate solution to the problems posed.

It has now surprisingly been found that by incorporating certain nano-sized
10 particles into the water borne coating composition comprising an organic polymeric binder, the leaching of water-extractable substances from a substrate into the coating, which becomes visible as stains on the surface of that substrate, is diminished or prevented when the coating composition is applied or during the service life of the coated article. Such water-extractable
15 substances are hereafter called "staining agents". The invention more specifically pertains to water borne coating compositions comprising an organic binder and at least one type of inorganic nano-particles as stain blocking agent. The inorganic nano-particles can be added to the water borne coating formulation during formulation. Optionally, the inorganic nano-particles are
20 combined with the organic binder to form a stable water borne binder composition. Preferably, said inorganic nano-particles have an electrical surface charge opposite to that of the staining agents to be blocked. Furthermore, the invention pertains to stable clear or pigmented water borne coating compositions comprising said organic water borne binder composition.

25

It is noted that the term nano-particles refers to nano-sized particles. Nano-sized denotes that at least one linear dimension has a mean size of less than one micron ($1 \mu\text{m} = 1 \times 10^{-6} \text{ m}$), more preferably less than 100 nanometres ($1 \text{ nm} = 1 \times 10^{-9} \text{ m}$), and most preferably from 0.1 nanometre to about 100
30 nanometres. There are nano-sized materials with the nano-size in three dimensions, in two dimensions (nano-tubes having a nano-sized cross-section,

ANR 3030 PDEP

4

but an indeterminate length), or in one dimension (nano-layers having a nano-sized thickness, but an indeterminate area). Preferred aspects of the present invention relate to layered materials which comprise nano-layers. The term "layered material" as used throughout the present specification is meant to
5 denote anionic clays, cationic clays, and layered hydroxy salts. It also includes modified forms of these layered materials, such as acid or base leached clays, pillared clays, and thermally treated layered materials that still have a layered structure. As the staining agents generally are of an anionic nature when present in the ionised form, preferably at least one type of nano-particles having
10 a cationic surface charge is employed.

It is noted that the use of zinc hydrotalcite as a UV light stabiliser in coating compositions is described in EP 0 982 356. The zinc hydrotalcite particles are mentioned to have a major diameter of 0.1 to 2 μm , and thickness of 0.01 to 0.3
15 μm , an aspect ratio of 2 to 200, and a secondary particle diameter of not more than 5 μm . In US 2002/0176982 the use of inorganic nano-particles, such as clay minerals and inorganic metal oxides, in coating compositions for imparting surface modifying benefits for all types of hard surfaces is disclosed. However, said documents do not relate to the problems underlying the present invention
20 and neither disclose nor suggest the use of the nano-particles in accordance with the present invention.

The anionic or cationic clays employed as the inorganic nano-particles may be used as such or may be exfoliated or intercalated. Intercalated clays consist of
25 a regular insertion of a polymer in between the clay layers. In exfoliated or delaminated clays the individual layers are separated and can be dispersed. The latter configuration is of particular interest because it maximises the surface area of the layers.

The clays which can be used according to the present invention may be
30 naturally occurring or synthetic. Preferably, cationic clays are used. Most preferably, anionic clays are employed in the water borne binder composition

ANR 3030 PDEP

5

according to the present invention. The inorganic polymeric nano-particles according to the present invention are either added to a water borne coating formulation during formulation, or are first combined with one or more organic polymeric binders forming a stable water borne binder composition, after which
5 a water borne coating composition is prepared.

Anionic clays

Anionic clays have a crystal structure consisting of positively charged layers built up of specific combinations of divalent and trivalent metal hydroxides
10 between which there are anions and water molecules. Trivalent metals (M^{3+}) that can suitably be present in the anionic clay include B^{3+} , Al^{3+} , Ga^{3+} , In^{3+} , Bi^{3+} , Fe^{3+} , Cr^{3+} , Co^{3+} , Sc^{3+} , La^{3+} , Ce^{3+} , and mixtures thereof. Suitable divalent metals (M^{2+}) include Mg^{2+} , Ca^{2+} , Ba^{2+} , Zn^{2+} , Mn^{2+} , Co^{2+} , Mo^{2+} , Ni^{2+} , Fe^{2+} , Sr^{2+} , Cu^{2+} , and mixtures thereof.

15 It should be noted that a variety of terms are used to describe the material that is referred to in this specification as an anionic clay. Hydrotalcite-like material and layered double hydroxide (LDH) are interchangeably used by those skilled in the art. In this specification we refer to these materials as anionic clays, comprising within that term hydrotalcite-like and layered double hydroxide
20 materials.

We have now found that anionic clays and, more preferably, layered double hydroxides (LDH) when incorporated into a water borne organic polymeric binder are very effective in the blocking of acidic extractable matter from a
25 variety of substrates. Layered double hydroxides (LDH) have the advantage that they can be incorporated into the polymeric binder without introducing haziness, and hence, clear stain blocking coatings can be produced.

In a particularly preferred embodiment of the present invention, layered double hydroxides of the pyroaurite-sjogrenite-hydrotalcite-group are employed in the
30 coating composition. These LDHs are based upon layers wherein magnesium cations are octahedrally surrounded by hydroxyl groups, which alternate with